

## THE POLYMERIZATION OF METHYL METHACRYLATE WITH A NEW TIN-BRIDGED YTROCENE/ $\text{Al}(\text{i-Bu})_3$ \*

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**Abstract:** A new catalyst composed of Tin-bridged ytrocene  $\text{Ph}_2\text{Sn}(\text{MeCp})_2\text{YCl}$  (MeCp = methylcyclopentadienyl) and  $\text{Al}(\text{i-Bu})_3$  was successfully developed for the polymerization of methyl methacrylate (MMA). Detailed study of factors (such as the molar ratio of Al/Cat., catalyst concentration, various solvents, temperature and time) influencing polymerization reaction indicated that the catalytic active species may be still somewhat stable at high temperature and still have a long catalytic lifetime.  $^1\text{H}$  NMR spectrum showed about 65% syndiotactic content in the polymethyl methacrylate (PMMA) prepared. From kinetic studies, the polymerization rate equation may be expressed as  $R_p = K_p[\text{Cat.}]^{2.4}$ . The overall activation energy of polymerization is  $20.9 \pm 3.1$  kJ/mol.

**Key words:** rare earth catalyst, ytrocene, heteronuclear metallocene, polymerization, methyl methacrylate, kinetics, lanthanocene

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### INTRODUCTION

Since the polymerization of methyl methacrylate (MMA) with rare earth catalysts was realized for the first time in 1991, a series of new rare earth catalyst systems such as  $\text{Nd}(\text{P}_{204})_3/\text{Al}(\text{i-Bu})_3$ ,  $\text{Nd}(\text{P}_{204})_3/\text{Al}(\text{i-Bu})_3/\text{CCl}_4$ ,  $\text{Nd}(\text{Oct})_3/\text{Al}(\text{i-Bu})_3$ ,  $\text{Ln}(\text{acac})_3/\text{BuMgCl}$ ,  $\text{Y}(\text{acac})_3/\text{Al}(\text{i-Bu})_3/\text{BuLi}$ ,  $\text{Nd}(\text{naph})_3/\text{BuLi}$ , and  $\text{Nd}(\text{O-i-Pr})_3/\text{Al}(\text{i-Bu})_3$  (Sun, 1997a; Sun et al., 1997b) were successfully developed. All the above-mentioned catalysts are typical Ziegler-Natta catalysts. In recent years, lanthanocene  $\text{Cp}_2^*\text{SmMe}$  or  $\text{Cp}_2^*\text{SmH}$  ( $\text{Cp}^*$  = penta-methylcyclopentadienyl) had also been used for the polymerization of MMA (Yasuda et al., 1993). Up to now, there is no report on MMA polymerization with tin-bridged metallocene.

Because metallocene catalyst can give tailored polymers with totally different structures and can control the polymer tacticity, molecular weight and its distribution, it has become a cur-

rently interesting topic in polyolefin synthesis. These strange behaviors arise from the defined structures in which carbon and silicon atoms are often used to bridge cyclopentadienyl ligands and render the rigidity of the ligand sphere in order to increase catalytic stereo-regularity and activity. Silanyl derivatives ( $-\text{SiR}_2-$ ) are particularly active in producing polymers with high molecular weight and/or high stereospecificity (Herrmann et al., 1996; Kaminsky, 1998) due to the large volume of the silicon atom. W. A. Herrmann reported a tin-bridged zirconocene as catalyst for the polymerization of ethylene (Herrmann et al., 1996). Both high activity and molecular weight of PE in his results stimulated us to select tin-bridged ytrocene as catalyst for investigation of MMA polymerization.

Here, we report the preliminary results of polymerization of MMA by  $\text{Ph}_2\text{Sn}(\text{MeCp})_2\text{YCl}/\text{Al}(\text{i-Bu})_3$  system. The structure of title ytrocene is shown in Fig. 1.

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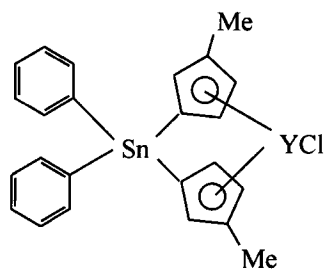


Fig. 1 The structure of title ytrocene

## EXPERIMENTAL DETAILS

### 1. Materials

MMA was washed with diluted NaOH until it became colorless, then dried over anhydrous  $\text{MgSO}_4$ , and finally distilled over calcium hydride under reduced pressure.  $\text{Ph}_2\text{Sn}(\text{MeCp})_2\text{YCl}$  was synthesized in the traditional manner (Chen et al., 1986) from anhydrous  $\text{YCl}_3$  and  $\text{Ph}_2\text{Sn}(\text{MeCpNa})_2$  prepared from the reaction of  $\text{Ph}_2\text{SnCl}_2$  with  $\text{MeCpNa}$  (Chen et al., 1986; Herrmann, 1996). All experiments for preparation of ytrocene were performed under an atmosphere of dry argon with rigid exclusion of air and moisture using standard Schlenk techniques.  $\text{Al}(\text{i-Bu})_3$  was purchased from Roth Company and used without any further purification. The solvents for the polymerization were refluxed over sodium benzophenone and used immediately after distillation.

### 2. Catalyst preparation and polymerization

The catalyst was prepared by adding stoichiometric amounts of  $\text{Al}(\text{i-Bu})_3$  to  $\text{Ph}_2\text{Sn}(\text{MeCp})_2\text{YCl}$  toluene solution and aged for defined time at room temperature.

The polymerization was carried out in an ampoule which was baked, vacuated and filled with pure argon for several cycles. The solvent, MMA and the catalyst solution were injected by hypodermic syringe sequentially into the ampoule at the polymerization temperature. The polymerization was terminated by adding ethanol containing 5% hydrochloric acid, and the polymer precipitated was washed with ethanol, dried at 50 °C under vacuum.

### 3. Measurement

The intrinsic viscosity of PMMA in  $\text{CHCl}_3$

was determined at 30 °C with an Ubbelohde-type viscometer. The viscosity-average molecular weight was calculated with the following equation:  $[\eta] = 4.3 \times 10^{-3} \bar{M}_\eta^{0.8}$  (ml/g) (Zheng, 1980). MWD values were measured by the GPC on a Waters Associates M730 at 25 °C using THF as eluent. The GPC was calibrated at 30 °C against standard polystyrene samples. The  $^1\text{H}$  NMR spectrum of PMMA was recorded at 60 °C on JEOL FX-90 using  $\text{CDCl}_3$  as the solvent.

## RESULTS AND DISCUSSION

Previous studies showed that not only traditional binary catalysts of rare earth complexes activated by aluminium alkyls, but also monocomponent rare earth metallocenes such as  $\text{Cp}_2^* \text{SmH}$  and  $\text{Cp}_2^* \text{SmCH}_3$  (Yasuda, 1993) can initiate efficiently the polymerization of MMA. We also found that  $\text{O}(\text{CH}_2\text{CH}_2\text{CpMe})_2\text{YCl}$ ,  $(\text{CH}_3)_2\text{Si}(\text{CpSiMe}_3)_2\text{NdCl}$ , ( $\text{Cp}$  = cyclopentadienyl) can initiate the polymerization of  $\epsilon$ -caprolactone (Sun et al., 1998) and MMA without any cocatalyst. In the present investigation, we tested the possibility of polymerization of MMA by monocomponent  $\text{Ph}_2\text{Sn}(\text{MeCp})_2\text{YCl}$ . Only a few oligomers were obtained no matter in solution or in bulk system at 60 °C. If some  $\text{Al}(\text{i-Bu})_3$  was added into the bulk system at 60 °C, the polymerization conversion increased significantly to more than 90%. Thus we decided to study the polymerization of MMA with title catalyst system.

### 1. Polymerization feature

#### (1) The effect of solvent

The polarity of solvents is one of the important factors that influence the polymerization behaviors due to the coordination of active species with solvents. The effect of solvent on the polymerization is summarized in Table 1.

Solvent	Conv. (%)	$\bar{M}_\eta (\times 10^4)$
Hexane	45.9	33.6
Toluene	38.8	20.6
THF	28.2	23.3

Polymn. conditions: MMA/Cat = 1 000 (molar ratio), 60 °C, 20 h, Al/Cat = 10 (molar ratio), MMA/Solv = 1 (volume)

Obviously, the polymerization conversion in THF (tetrahydrofuran) was the lowest among the investigated solvents, but the  $\bar{M}_\eta$  of PMMA obtained from THF was not so low. This result is similar to the polymerization of MMA by Nd(O-*i*-Pr)<sub>3</sub> - Al(*i*-Bu)<sub>3</sub> (Sun, 1997a). These facts illustrate that polar solvent does not influence the lifetime of active species. The coordination of polar solvent with active species hinders the coordination of monomer and leads to a drop in the rate of chain propagation, but on the other hand, it might stabilize the active species. Hexane can precipitate the polymer produced which might decrease the chain termination caused by the collision of active species, thus yielding higher conversion and higher  $\bar{M}_\eta$  of PMMA.

#### (2) The effect of Al/Cat. ratio

In the Ziegler-Natta catalyst systems, aluminium alkyls have been most extensively used as cocatalyst. The functions of aluminium alkyls are not only to activate the transitional metal complexes, but also to eliminate trace impurities such as moisture, oxygen, etc. which hinder polymerization. Fig. 2 indicates the important role of Al(*i*-Bu)<sub>3</sub>. The conversion and  $\bar{M}_\eta$  increase smoothly as the molar ratio of Al/Cat increases. When Al/Cat. = 10, the polymerization conversion reaches to more than 60% and the  $\bar{M}_\eta$  of PMMA exceeds  $1.0 \times 10^{-6}$ . When the molar ratio of Al/Cat. was larger than 10, i.e. 15, the PMMA prepared was unexpectedly insoluble in CHCl<sub>3</sub>, which hinders the characterization of PMMA at present.

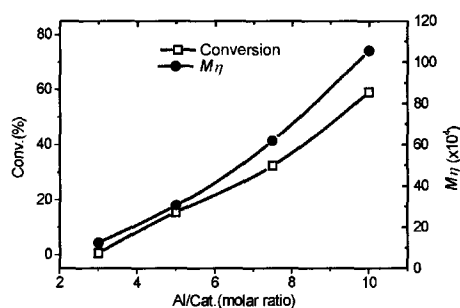


Fig. 2 Effect of the Al(*i*-Bu)<sub>3</sub>/Cat. (molar ratio)

Polymn. conditions; MMA/Cat = 1000 (molar ratio), 60 °C, 25h, bulk

#### (3) The effect of MMA/Cat ratio

Table 2 shows that there was a suitable MMA/Cat. molar ratio for the polymerization.

MMA/Cat. < 1000 yielded high molecular weight PMMA at satisfactory conversion (> 60%). The molecular weight of PMMA increased with increase of the MMA/Cat. value because each active center could have more monomer molecules and got a longer polymer chain. When the molar ratio of MMA/Cat. was higher than 1000, both the polymerization conversion and  $\bar{M}_\eta$  of PMMA decreased remarkably, probably because of the consumption of a part of the catalyst for elimination of impurities existing in the polymerization system.

Table 2 The effect of catalyst concentration

MMA/Cat	Conv. (%)	$\bar{M}_\eta (\times 10^4)$
500	99.0	68.6
1000	59.2	105.6
2000	21.4	73.9
3000	10.6	35.2

Polymn. conditions; 60 °C, 25h, Al/Cat = 10 (molar ratio), bulk

#### (4) The effect of temperature

The dependence of the polymerization on temperature was examined in detail from 0 °C to 60 °C. Fig. 3 shows that high temperature like 60 °C is favorable for obtaining good polymerization conversion. This may be attributable to the faster chain propagation at higher temperature caused by the increase of active monomer molecules. From the increase tendency of  $\bar{M}_\eta$  of PMMA plotted in Fig. 3, it can be seen that the active species was still stable at high temperature. This phenomenon is different from the polymerization results of MMA with Nd(naph)<sub>3</sub>-BuLi, in which both polymerization conversion and  $\bar{M}_\eta$  of PMMA dropped remarkably with the increase of

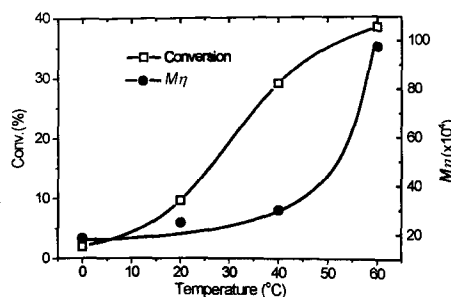


Fig. 3 Effect of the polymerization temperature

Polymn. conditions; MMA/Cat = 1000 (molar ratio), 20 h, Al(*i*-Bu)<sub>3</sub>/Cat = 10 (molar ratio), bulk

temperature (Liu et al., 1996). The difference indicates that tin-bridged ligand might stabilize the active species.

#### (5) The effect of time

Fig. 4 shows that both the polymerization conversion and  $\bar{M}_n$  of PMMA increased gradually within the polymerization time tested. It is noteworthy that the polymerization conversion increased rapidly after it reached 40%. It is similar to the auto acceleration in the radical polymerization of MMA (O'dian, 1981). On the other hand, the  $\bar{M}_n$  of PMMA increased linearly with increased polymerization conversion. It indicates that active species have a long lifetime. In order to clarify living polymerization feature, a second equal amount (1 ml = 0.936 g) of MMA was added into the polymerization system after 20hr and the polymerization was continued for another 10hr. At the end of this polymerization, 1.4g PMMA was obtained. This positive evidence proves again the stability of active species of tin-bridged ytrocene.

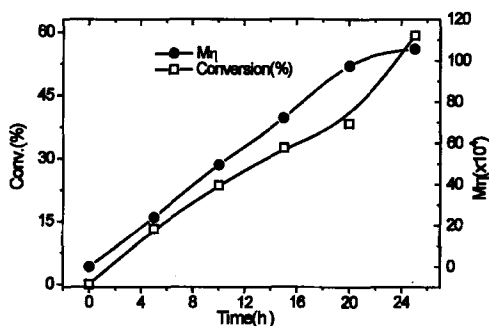


Fig. 4 Effect of polymerization time

Polymn. conditions; MMA/Cat. = 1 000 (molar ratio), 60 °C, Al(i-Bu)<sub>3</sub>/Cat = 10, bulk

## 2. The characterization of PMMA

### (1) <sup>1</sup>H NMR

As we know, PMMA has chiral centers which lead to formation of isotactic(I), syndiotactic(s) and atactic(h) stereoisomers that influence greatly the mechanical properties. Therefore, <sup>1</sup>H NMR was used for investigation of stereoregularity of PMMA prepared. The resonance peaks of CH<sub>3</sub> in Fig. 5 at 0.92, 1.02 and 1.20 represent isotactic, atactic and syndiotactic polymers respectively. The result shows that the content of syndiotactic PMMA was about 65%, which was in accordance with the results ob-

tained from IR determination.

### (2) GPC

As shown in Fig. 6, all GPC (omitted) spectra determined indicate one peak. It suggests that the polymerization might be carried out with one active species.

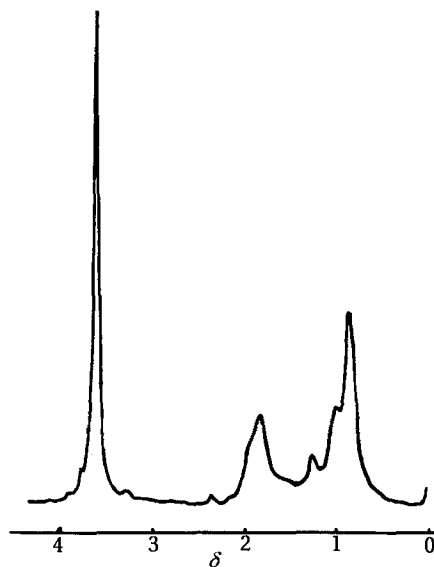


Fig. 5 <sup>1</sup>H-NMR spectrum of PMMA

Polymn. conditions; MMA/Cat = 1000 (molar ratio), 40 °C, 25h, Al/Cat = 10.

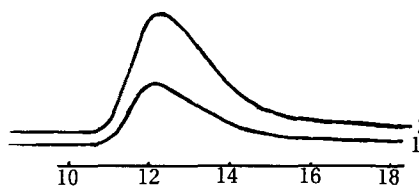


Fig. 6 GPC spectra of PMMA

Polymn. conditions; 1. MMA/Cat = 1000 (molar ratio), 60 °C, 25h, Al/Cat = 10, bulk; 2. MMA/Cat = 3000 (molar ratio), 60 °C, 25hr, Al/Cat = 10, bulk.

## 3. Polymerization kinetics

The kinetics of MMA polymerization in toluene with Ph<sub>2</sub>Sn(MeCp)<sub>2</sub>YCl/Al(i-Bu)<sub>3</sub> were studied in detail by the weight method. Fig. 7 shows some curves of the time vs the conversion of polymerization carried out with different molar ratio of MMA/Cat. The obvious linear relationship between conversion and polymerization time indicates the zero order of the monomer concentration. However, from the slope of Fig. 8, the R<sub>p</sub> is 2.4 (the relative coefficient is 0.99) reaction order of the catalyst concentration, so the polymerization rate equation can be written as R<sub>p</sub>

$$= K_p [\text{catalyst}]^{2.4}.$$

The polymerization was carried out at 30 °C, 50 °C, 60 °C. According to the Arrhenius Law,

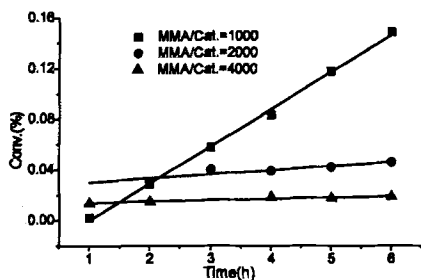


Fig. 7 Relationship between polymn. conv. and time  
Polymn. conditions: Al/Cat = 10 (molar ratio), 60 °C,  
MMA/Solv = 1 (volume)

we can get the overall activation energy of polymerization as  $20.93 \pm 3.1$  kJ/mol (Fig. 9, the relative coefficient is 0.98).

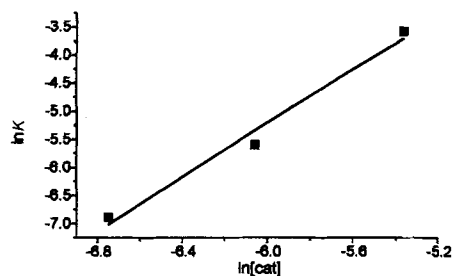


Fig. 8 Reaction order of catalyst

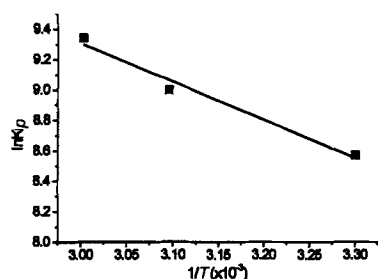


Fig. 9  $E_p$  calculated from Arrhenius formulation  
Polymn. conditions: Al/Cat = 10 (molar ratio), MMA/Cat.  
= 1 000 (molar ratio), MMA/solv. = 1 (volume), 60/50/  
30 °C

## CONCLUSIONS

A new rare earth metallocene catalyst of  $\text{Ph}_2\text{Sn}(\text{MeCp})_2\text{YCl}/\text{Al}(\text{i-Bu})_3$  was developed for the polymerization of MMA. More than 90% high polymerization conversion and over  $1.0 \times 10^6$  of PMMA were obtained in bulk polymerization. The syndiotactic content of PMMA prepared at 40 °C was about 65%. From the stability at high temperature and long lifetime of active species, it can be concluded that tin-bridged cyclopentadienyl ligand can stabilize the catalytic active species.

## References

- Chen, S.S., Zhang, Z.Z., Wang, X.K., et al., 1986. Handbook of organometallic compounds synthesis. Chemical Industry Press, Beijing, p.124 - 139, 292 - 297.

- Herrmann, W.A., Morawietz, J.A., Herrmann, H.F., et al., 1996. Tin-bridged ansa-metallocenes of zirconium: synthesis and catalytic performance in olefin polymerization. *Journal of Organometallic Chemistry*, **509**: 115.
- Kaminsky, W., 1998. Highly active metallocene catalysts for olefin polymerization. *J. Chem. Soc., Dalton Trans.*, 1413 - 1418.
- Liu, J.F., Shen, Z.Q., Sun, J.Q., 1996. Polymerization of methyl methacrylate with a homogenous neodymium catalyst:  $\text{Nd}(\text{naph})_3\text{-BuLi}$ . *Eur. Polym. J.*, **32**(7): 883.
- Odian, J., 1981. Principles of Polymerization. 2nd. ed., John Wiley&Sons Inc., New York, p.272.
- Sun, J.Q., 1997a. The polymerization of methyl methacrylate with a new  $\text{Nd}(\text{O-i-Pr})-\text{Al}(\text{i-Bu})_3$  catalyst system. *Chemical Research in Chinese Univ.*, **13**(4): 344.
- Sun, J.Q., Pan, Z.D., 1997b. Polymerization of methyl methacrylate with novel  $\text{Ln}(\text{acac})_3\text{-n-BuMgCl}$ . *Chinese J. of Appl. Chem*, **14**(2):1.
- Sun, J.Q., Pan, Z.D., 1998. Ring-opening polymerization of  $\epsilon$ -caprolactone by lanthanocene catalysis. *Chinese J. Of Polymer Sci.*, **16**(4): 297.
- Yasuda, H., 1993. Characteristics of rare earth systems as polymerization initiators. *Prog. Polym. Sci.*, **18**: 1097.
- Zheng, C.R., 1980. Molecular weight and molecular weight distribution of polymers. Chem. Ind. Press, Beijing, p.604.